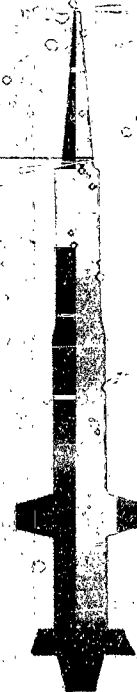


401908

CATALOG ACT-1
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CORPORATION





April 15, 1963

Gentlemen:

Progress Report #13 on Glass Surface Chemistry for Glass Fiber Reinforced Plastics for the period March 1 through March 31, 1963 is enclosed.

Bond life studies with Owens-Corning's HTS finish indicated that this finish is comparable to other successful finishes in so far as wet strength retention is concerned. Further bond life tests indicate that aluminum does not have good wet strength retention with the present day finishes. The bond strength test has been modified to the extent that we feel the test can be used to accumulate data on glass surface variations versus bond strength.

Very truly yours,

A. O. SMITH Corporation

A handwritten signature in cursive script that reads 'F. W. Nelson'.

F. W. Nelson, Director
Ceramic Research and Development

FWN:mk

PROGRESS REPORT #13
on
GLASS SURFACE CHEMISTRY FOR GLASS FIBER REINFORCED PLASTICS
for the period
March 1, through March 31, 1963

I. Summary

Bond life of Owens-Corning HTS finished E glass was more than 12 days in 190°F water and is still on test. Wetting of HTS glass, as determined by the captive bubble technique, was similar to epoxy resin coated glass. The contact angle was 81-90, indicating a high degree of non-wetting by water.

Bond life of aluminum was also studied as part of the exploratory work on bond strength testing. Bond life of as-rolled aluminum, whether treated with A-1100 or not, was poor (less than one day). Although metal coatings might be effective in preventing strength deterioration of glass fibers due to moisture, development work would apparently be needed to obtain effective moisture-resistant bonding of epoxy resin to the aluminum coated glass fibers. Other metals might also be ineffective with respect to wet bonding unless a suitable finish was developed.

Recent work has indicated that the bond strength test could be modified to minimize the effect of stresses created by the shrinkage of the high expansion resin during curing. Heretofore the bond specimen was made by casting a column of resin on the glass surface. This 100% resin column created excessive stresses during curing of the specimen. These stresses have been reduced through the addition of chopped E glass fibers to the resin. A thin layer of 100% resin is poured on the glass surface prior to casting the column. This maintains the normal resin-to-glass interface.

The elimination of the abnormal stresses should produce a more uniform specimen and, in addition, should decrease the number of resin failures. This modified test will be used to complete the evaluation of the bond strength for the various glass surfaces. The cure cycle will also be condensed to increase the capacity for specimen testing from 20 to 50 per week. We believe that this schedule will permit the testing of all types of glass surfaces in the limited time available. However, it will not permit further exploratory work for developing a bond strength test that consistently produces failure at the resin-to-glass interface. This is an idealistic test that may or may not be attainable. The present test should be more than adequate to supply us with the necessary data for evaluating the effect of glass surface on the bond strength.

Testing of bond strength by the chain method showed that bonding to the chemically cleaned, optical flat E glass surface was less effective than to the as-cast surface, whether treated with A-1100 or not. It was also established with 98 per cent confidence that treatment of the optical flat surface with A-1100 caused a slight increase in bond strength.

II. Bond Life and Wetting Studies

A. HTS Finished E Glass

As-cast E glass samples were coated by Owens-Corning with their HTS finish. Owens-Corning expected difficulty in controlling the finish thickness due to the use of a bulk specimen instead of glass fibers. The HTS coating on the as-cast samples was sufficiently thick to be visible to the naked eye. The coating was also tacky and cotton fuzz from the shipping container adhered to the samples. The cotton was removed with compressed air. Some of the samples were damaged in shipping, but enough samples remained for testing bond life and wetting.

Bond life of HTS finished E glass was more than 12 days (Table I). Testing will continue. Wetting of the HTS finished glass, as determined by the captive bubble technique, was similar to epoxy resin coated glass. The contact angle was 81-90, indicating a high degree of non-wetting by water (Table II).

B. Bonding to Aluminum Surfaces

A possible test specimen for bond strength consisted of an aluminum rod bonded perpendicular to the optical flat glass. Since it is intended that the test be used eventually for studying wet environments, the permanency of the epoxy resin-aluminum bond needed to be established. Other reasons for studying bonding to aluminum also appeared:

1. Various investigators^(1, 2, 3) have suggested protecting the glass fibers from strength deterioration in moisture by coating with metals. Although not doubting the effectiveness of a continuous metal coating, it would seem that another important consideration is the compatibility of the metal with epoxy resin.
2. Past experience indicated aluminum to be the only metal effectively bonded to epoxy resin, and little effort was needed to re-test this bonding.

Bond life of the as-rolled aluminum treated with and without A-1100 was less than one day (Table I). Bonding of the mirror-type aluminum was less than one day but was improved by A-1100. Roughening the aluminum by lightly sandblasting promoted bond life.

Aluminum surfaces are known to vary widely depending on the amount of aluminum oxide formed⁽⁴⁾, but it is believed that the as-rolled surface would more nearly correspond to the aluminum coating on a glass fiber. Therefore, the resistance of the bond to destruction by water in aluminum-coated glass fiber composites was indicated to be poor. Apparently, development work would be needed to obtain moisture-resistant bonding of epoxy resin to aluminum coated glass fibers. Other metals might also be ineffective with respect to the wet bond unless a suitable finish was developed. It is known that considerable art is involved in bonding metals to glass surfaces^(5, 6).

C. Bond Life of Optical Flat E Glass Surfaces

Bond life of chemically cleaned, optical flat E glass surfaces (marble specimen) treated with A-1100 was less than the as-cast glass surface (Table I). This result is being repeated for the optical flat surface ground on an E glass plate.

The alkali-deficient optical flat surface failed prematurely (11 days). These samples were prepared by grinding optical flat a 1/2 inch diameter spot on E glass marbles. A sharp edge (discontinuity) existed between the flat surface and the remaining surface of the marble. After acid leaching the marble, failure was in the glass. The entire glass surface was torn from the marble by the epoxy resin coating. The acid leached surfaces on the as-cast samples (not marbles) that had been ground flat have not exhibited failure after 32 days. These specimens had little discontinuity between the flat and the as-cast surface. This result indicated that the glass surface was weakened by the acid leaching. It is known that acid leaching reduces the strength of E glass fibers⁽⁷⁾.

III. Bond Strength Studies

A. Exploratory

As in the past, a considerable portion of the month was spent evaluating possible test methods and refinements of the present bond strength test. One possible test method consisted of bonding an aluminum rod perpendicular to the glass surface. The test was abandoned because of difficulty in obtaining a thin, uniform joint. Reproducibility was poor.

A similar test, instead of using a foreign material such as aluminum, used glass fibers impregnated with resin that were packed into a glass tube. The glass fibers were oriented perpendicular to the glass surface. The resin was B-staged 16 hours at room temperature. The rod of glass fibers and resin was then glued to the glass surface. The test was abandoned because uniformity of joint thickness was difficult; specimen preparation was also time-consuming.

However, the incorporation of glass fibers was effective in diminishing the resin and glass failures and increasing the bond failures. The fibers served as reinforcement to prevent resin failure. The glass fibers also diminished the resin shrinkage stress normal to the glass surface. It is planned to incorporate glass fibers in the present bond strength chain test method (Progress Report #11). A resin film will be placed on the glass surface and the remaining volume of the Teflon gasket will be filled with chopped E glass fibers and resin.

No further exploratory studies are planned at the present time. The limited funds and time make testing by the present bond strength chain method imperative if the task is to be completed. Moreover, past work has shown little promise that a bond strength test can be developed that consistently produces bond failures and reproducible results for all types of E glass surfaces. For example, the present test produced a majority of bond failures on the chemically cleaned glass surface. However, acid leaching weakened the glass surface (alkali-deficient) and the majority of failures occurred in the glass and not in the bond (Progress Report #12). Room temperature curing the resin (Epon 828 with diethylene triamine) weakened the resin and failures, therefore, occurred in the resin (Progress Report #7). The A-1100 treatment of chemically cleaned, optical flat E glass surfaced produced more failures in the resin than in the bond.

Rather than be faced with the formidable task of developing a test for consistent bond failures, future testing will be concerned with the frequency of resin, glass, or bond failures and the relative stress level for each type of failure (see Figures 1 and 2). Approximately 30 samples per variable will be required. The present test design will be frozen, except for the modification using glass fibers. It is also planned to reduce the curing schedule from the present NOL ring cure to the shorter 1 hour at 250°F and 1 hour at 350°F. A correlation of cure schedules with bond strength is planned. The reduced cure time will increase the capacity for specimen testing from 20 to 50 per week.

B. Bond Strength by the Butt-Joint Chain Method

Figures 1 and 2 summarize testing to date on the chemically cleaned as-cast and optical flat E glass surfaces with and without A-1100. The distribution plots show the relative tensile strength for each class of failure location. The location of failure was arbitrarily divided in units of 25 per cent of bond failure. Failures, such as 60 per cent resin and 40 per cent bond, were classed as 50 per cent resin and 50 per cent bond. Failures, such as 65 per cent resin and 35 per cent bond, were grouped as 75 per cent resin and 25 per cent bond failure. These curves were somewhat misleading in that failures in the glass occurred more frequently than shown. Resin-glass failures, for example, were not plotted. Failures having all three types, glass, resin, and bond, were grouped with resin and bond failures if the total area of glass failed was less than as estimated 15 per cent of the 1/8 inch diameter bond area.

Nevertheless, the data plotted was significant and the following results were derived:

1. Bonding to optically flat E glass surfaces was less effective than to the as-cast surface, whether treated with A-1100 or not. This was established on the 99.9 per cent confidence level. Bond strength of the chemically cleaned as-cast glass surface was 990 psi ($\sigma = 210$) but was only 400 psi ($\sigma = 130$) to the optical flat surface. Bond strength after A-1100 treatment was 1325 psi ($\sigma = 190$) for the as-cast surface and 575 psi ($\sigma = 96$) for the optical flat surface.
2. Treatment with A-1100 slightly improved the bond strength using the optical flat surface. This was established with 98 per cent confidence.
3. Treatment with A-1100 on either the as-cast or the optical flat glass surface caused the failure to occur more frequently in the resin. This result correlates with the improvement in bond strength with A-1100 (Result 2).
4. The highest relative tensile strength resulted when the failure occurred in the resin.
5. The data did not show whether the bond was the weak link, but only the probability for bond failures. For example, in Figure 1, a total of 38 specimens were tested for the untreated surface and 40 for the A-1100 treated surface. The probability of 100 per cent bond failure in the untreated specimen was 10 divided by 38 or 26 per cent. The same probability for any type of failure can also be

calculated for the optical flat surface. A total of 33 specimens were tested for the untreated surface and 31 for the A-1100 treated surface. For the untreated optical flat surface (Figure 2), the probability of 100 per cent bond failure was 27 per cent.

Acknowledgment

Thanks is extended to the Owens-Corning Fiberglas Corporation for their co-operation in preparing samples.

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5. Otto, W. et. al., "U. S. 2,772,987" (Dec. 4, 1956).
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TABLE I

BOND LIFE STUDIES BY FLAT PLATE TEST
Days to Failure Determined Visually

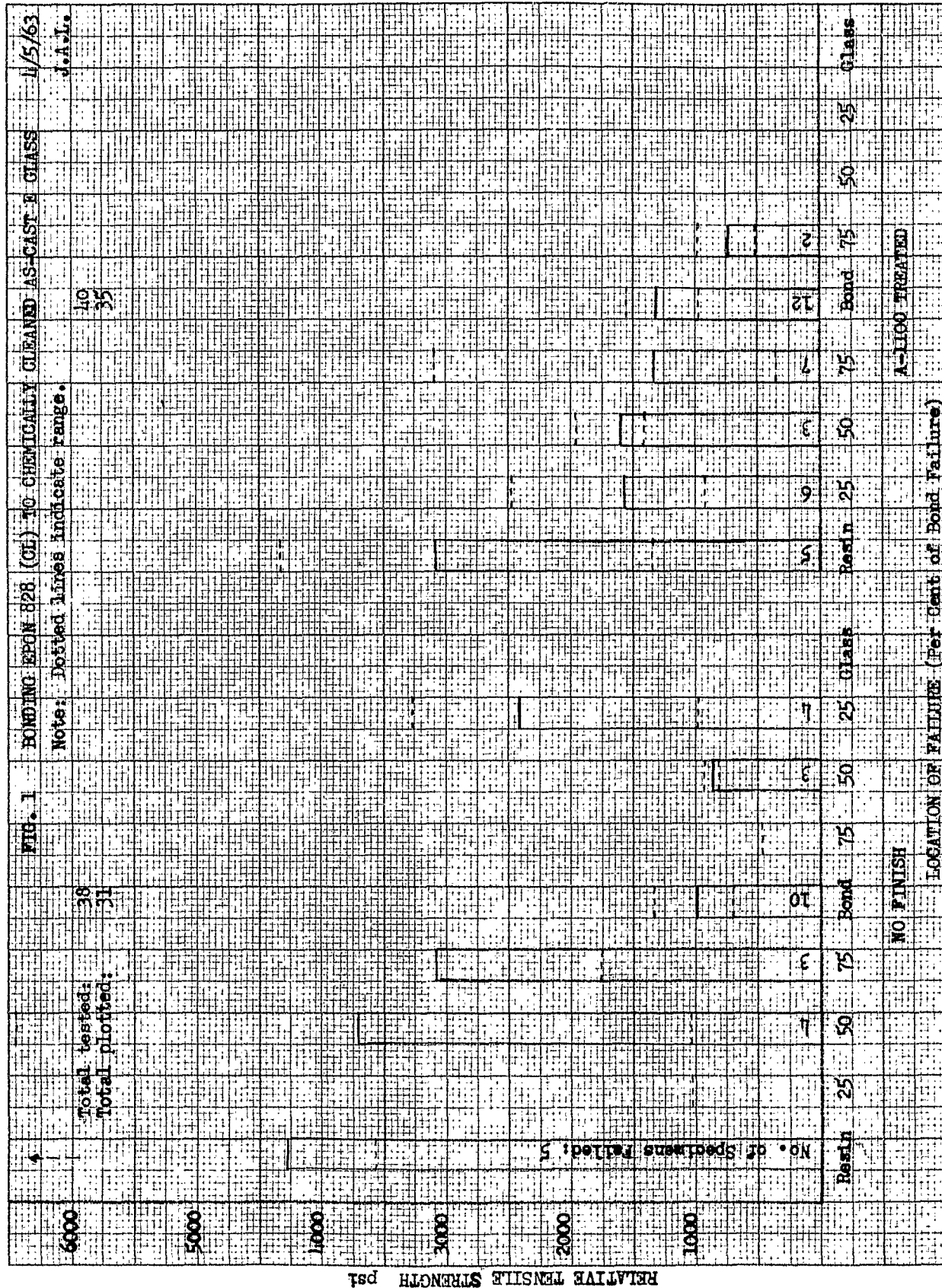
Type of Surface	Treatment	Days to Failure
AS-CAST E GLASS		
Chemically cleaned	None	1
Chemically cleaned	A-1100	186
Contaminated	None	1
Contaminated	A-1100	186*
Contaminated	HTS	12*
Alkali-deficient (prepared in air)	None	83*
Alkali-deficient	None	230
Alkali-deficient	A-1100	203*
Alkali-rich	None	12
Alkali-rich	A-1100	49
Lightly sandblasted	None	7
Lightly sandblasted	A-1100	182*
Cleaved in resin	None	1
Degassed	None	1
Degassed	1/2% A-1100	55
Degassed	10% A-1100	80
Degassed	1/2% Z-6040	206*
As-Cast (Annealed)	None	1
Chemically cleaned, heated to 190°F before resin applied.	None	1
OPTICALLY FLAT E GLASS		
Chemically cleaned (marbles)	None	1
Chemically cleaned (marbles)	A-1100	18
Chemically cleaned	A-1100	32*
Alkali-Deficient (marbles)	None	11
Alkali-Deficient (marbles)	A-1100	31*
Alkali-Deficient	None	21*
Alkali-Deficient	A-1100	21*
Lightly sandblasted (marbles)	None	28*
Lightly sandblasted (marbles)	A-1100	28*
ALUMINUM SURFACES		
As-rolled	None	1
As-rolled	A-1100	1
Mirror finish	None	1
Mirror finish	A-1100	4*
Lightly sandblasted	None	19*

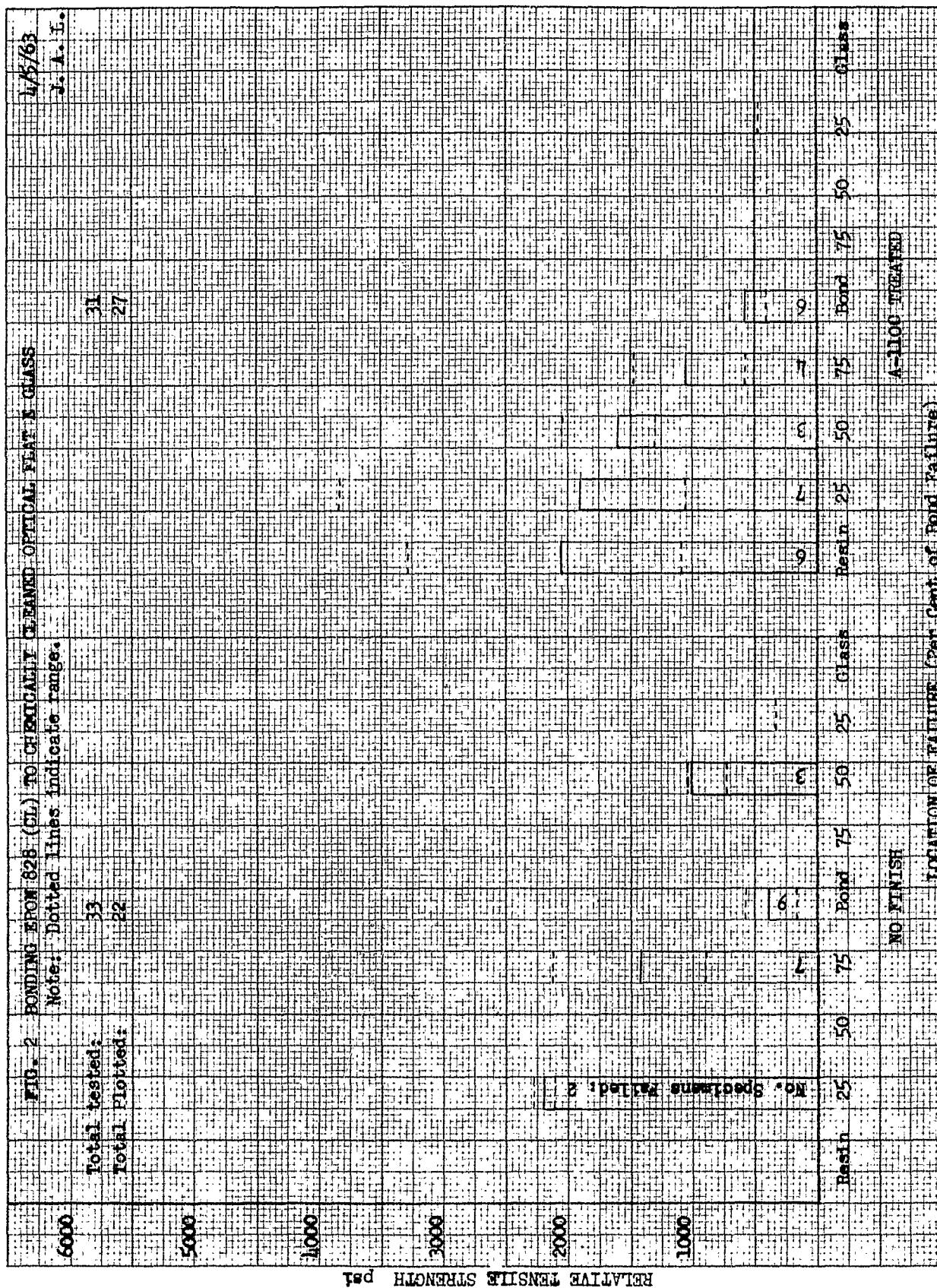
*Still on test.

TABLE II
WETTING STUDIES
Contact Angle By Captive Bubble Technique

Type E Glass Surface	Treatment	System		
		Air-H ₂ O	Air-A-1100 in H ₂ O	Air-Epoxy Resin
AS-CAST				
Chemically cleaned	None	Nil	38	Nil
Chemically cleaned	A-1100	63	--	Nil
Chemically cleaned	HTS	81-90	--	Nil
Contaminated	None	44	39	Nil
Contaminated	A-1100	61	--	Nil
Alkali-deficient	None	Nil	Nil	Nil
Alkali-deficient	A-1100	Nil	--	Nil
Alkali-rich	None	Nil	Nil	Nil
Alkali-rich	A-1100	Nil	--	Nil
Lightly sandblasted	None	Nil	Nil	Nil
Lightly sandblasted	A-1100	Nil	--	Nil
Degassed	None	Nil	46	Nil
Degassed	1/2% A-1100	63	--	Nil
Degassed	10% A-1100	63	--	Nil
Degassed	1/2% Z-6040	63	--	Nil
Cleaved in resin	None	Nil	--	--
OPTICALLY FLAT				
Chemically cleaned	None	Nil	--	Nil
Chemically cleaned	A-1100	63	--	Nil
Alkali-deficient	None	Nil	--	--
Alkali-deficient	A-1100	Nil	--	--
Lightly sandblasted	None	Nil	--	--
Lightly sandblasted	A-1100	Nil	--	--

Note: Complete wetting by the liquid corresponds to a contact angle of nil.





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